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(54) Title of the Invention: Optical Glass Filter, and Method for Calibrating Transmissivity or Absorbance in Ultraviolet Region Using Same

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SPECIFICATION

1. **Title of the Invention**

Optical Glass Filter, and Method for Calibrating Transmissivity or Absorbance in Ultraviolet Region Using Same

2. **Claims**

1. An optical glass filter for calibrating transmissivity or absorbance in the ultraviolet region, characterized by the addition of 0.001 to 0.2 wt% CeO_2 to fluorophosphate glass consisting of 8 to 40 wt% P_2O_5, 5 to 35 wt% AlF_3, 30 to 75 wt% RF_2 (R is at least one metal selected from among Ba, Sr, Ca, Mg, and Zn), 0 to 40 wt% R'F (R' is at least one metal selected from among Li, Na, and K), and 0 to 15 wt% $R''F_m$ (R'' is at least one metal selected from among La, Y, Gd, Si, B, Zr, and Ta; and m is the valence of the metal R''), wherein metal oxides may be substituted for up to 70% of the total amount of the metal fluorides AlF_3, RF_2, R'F, and $R''F_m$ as required.

2. A method for calibrating transmissivity and absorbance in the ultraviolet region using the optical glass filter according to Claim 1.

3. **Detailed Description of the Invention**

[Field of Industrial Utilization]

The present invention relates to an optical glass filter and to a method for calibrating transmissivity and absorbance in the ultraviolet region using this filter.

[Prior Art]

The measurement of concentration by absorptiometry makes use of a characteristic whereby substances have a unique absorption coefficient at a specific wavelength, and involves specifying a substance by wavelength graduation, and measuring the concentration of the substance in the transmissivity or absorbance graduations.

Spectrophotometers based on absorptiometry are widely used as pollution gauges for quantifying contaminants in the water or soil, and as pharmaceutical analyzers and clinical analyzers, and ensuring high performance and reliability in these analyzers is of great importance.

At present, ND (Neutral Density) glass filters, metal film filters, and potassium dichromate solution filters are used to calibrate the transmissivity and absorbance graduations of these spectrophotometers. However, the above-mentioned ND glass filters include a large quantity of coloring ions of iron, cobalt, and so forth, so they do not transmit light with a wavelength shorter than 350 nm, and cannot be used to calibrate transmissivity or absorbance in the ultraviolet region. Metal film filters are used to calibrate transmissivity and absorbance in the ultraviolet region, but a drawback is that reflected light becomes stray light and lowers the reliability of the measured values. Potassium dichromate solution filters are also used to calibrate transmissivity or absorbance in the ultraviolet region, but their drawbacks include the following.

(1) Because they are solution filters, they can only be used once (cannot be reused).

(2) Preparation of the solution is difficult and requires considerable skill.

(3) There is a great deal of variance in measured values attributable to solution preparation.

(4) High-purity potassium dichromate, perchloric acid, and other such reagents are necessary.

(5) The preparation of the solution requires a high-precision scale, chemical analyzer, and other such equipment.

(6) Because potassium dichromate is a designated pollution substance, the waste solution must be treated.

[Problems Which the Invention is Intended to Solve]

It is therefore an object of the present invention to provide an optical filter for calibrating transmissivity or absorbance in the ultraviolet region, which is free from the drawbacks of the above-mentioned conventional filters for calibrating transmissivity or absorbance, and which offers excellent precision, ease of handling, and so forth, and can be used over a relatively wide range of wavelengths, including the short wavelength region under 350 nm

[Means Used to Solve the Above-Mentioned Problems]

The stated object of the present invention is achieved by adding a specific amount of CeO_2 to fluorophosphate glass having the following specific composition.

Specifically, the optical glass filter of the present invention for calibrating transmissivity or absorbance in the ultraviolet region is characterized by the addition of 0.001 to 0.2 wt% CeO_2 to fluorophosphate glass consisting of 8 to 40 wt% P_2O_5, 5 to 35 wt% AlF_3, 30 to 75 wt% RF_2 (R is at least one metal selected from among Ba, Sr, Ca, Mg, and Zn), 0 to 40 wt% R'F (R' is at least one metal selected from among Li, Na, and K), and 0 to 15 wt% $R''F_m$ (R" is at least one metal selected from among La, Y, Gd, Si, B, Zr, and Ta; and m is the valence of the metal R"), wherein metal oxides may be substituted for up to 70% of the total amount of the metal fluorides AlF_3, RF_2, R'F, and $R''F_m$ as required.

The present invention will now be described in detail.

First, the reasons for the quantitative limits on the various components of the fluorophosphate glass that serves as the matrix in the optical glass filter of the present invention will be described.

The glass will be unstable if the P_2O_5 content is less than 8%, but if 40% is exceeded the chemical resistance will suffer, so the amount of P_2O_5 is limited to between 8 and 40%.

Chemical resistance will suffer if the AlF_3 content is less than 5%, but if 35% is exceeded the glass will be unstable, so the amount of AlF_3 is limited to between 5 and 35%.

Glass of sufficient stability will not be obtained if the RF_2 content is either less than 30% or over 75%, so the amount of RF_2 is limited to between 30 and 75%.

If the R'F content is over 40%, not only will the chemical resistance suffer, but the molten R'F will also volatilize excessively, so the amount of R'F is limited to between 0 and 40%.

If the $R''F_m$ content is over 15%, not only will the glass be unstable, but it will not melt well, so the amount of $R''F_m$ is limited to between 0 and 15%.

Up to 70% of the total amount of the above-mentioned metal fluorides AlF_3, RF_2, R'F, and $R''F_m$ can be substituted with metal oxides.

The optical glass filter of the present invention for calibrating transmissivity or absorbance is based on fluorophosphate glass containing the various components listed above in their respective limited amounts, to which CeO_2 is added in an amount of 0.001 to 0.2 wt%, but if the CeO_2 is present in the form of Ce^{3+} in the base glass, the absorption peak that is usually near 350 nm with silicate glass makes a surprising shift to 300 nm or less, and has a smooth transmissivity curve all the way from 200 to 300 nm, and as a result it is possible to calibrate transmissivity or absorbance over a relatively wide range of wavelengths in the short wavelength region under 350 nm.

The above absorption pattern does not change greatly as a result of varying the type or content of the divalent component in the base fluorophosphate glass composed of metal fluorides and P_2O_5 in the compositional ranges given above, and remains the same whether the amount of divalent component is reduced or the amount of univalent component or of trivalent or other high-valence component is increased. Therefore, it is possible to produce a filter having similar absorption characteristics over a wide compositional range, but in order to produce a filter with good chemical resistance and few manufacturing obstacles, it is particularly favorable to use a fluorophosphate glass composed of metal fluorides and P_2O_5 within the following compositional ranges.

	Wt %
P_2O_5	10~30
AlF_3	8~30
$BaF_2+SrF_2+CaF_2+MgF_2$	50~70
BaF_2	0~40
SrF_2	0~40
CaF_2	0~30
MgF_2	0~20
LiF	0~20
LaF_3+YF_3	0~8

(It is also possible for up to 50% of the total amount of metal fluorides to be substituted with metal oxides.)

It is possible to vary the transmissivity curve as dictated by the application by adding minute amounts of transition metal oxides to the above-mentioned base fluorophosphate glass, such as up to 0.6 wt% Cr_2O_3, up to 0.01 wt% Fe_2O_3, up to

0.01 wt% Co_2O_3, up to 0.01 wt% NiO, up to 0.01 wt% V_2O_5, up to 0.05 wt% MnO_2, up to 0.05 wt% CuO, and up to 0.5 wt% Eu_2O_3. A known defoaming agent such as As_2O_3, fluorine, or chlorine can also be used. However, PbO, TiO_2, Nb_2O_5, WO_3, and other such compounds having extremely strong absorption in the ultraviolet region must not be contained.

The transmissivity or absorbance graduations of the filter of the present invention for calibrating transmissivity or absorbance in the ultraviolet region, obtained by adding CeO_2 to the above-mentioned base fluorophosphate glass, are calibrated by the following method. The power is turned on to a spectrophotometer, and after the unit has stabilized, the 0% and 100% transmissivity adjustments are made, and then the measurement wavelength and bandpass are set. The designated wavelength and bandpass indicated on the calibrating optical glass filter are used here. The control light flux is air, and the calibrating optical glass filter is mounted on the sample light flux side. In the calibration of transmissivity or absorbance graduations, the wavelength graduations must be calibrated ahead of time. This calibration of wavelength graduations is accomplished using a wavelength calibration filter and the bright line wavelength of a low-pressure quartz mercury vapor lamp or deuterium lamp. With a spectrophotometer having a temperature control unit, the temperature is held at 23.5°C, and transmissivity is measured after it has been confirmed that the temperature is stable. To calibrate a spectrophotometer, the transmissivity measurement of the calibrating optical glass filter mounted thereto is repeated three times. The average thereof is used as the measured value, the difference from the value of the calibrating optical glass filter (subsequently determined by a public agency) is found, and this is used as the instrumental error of this spectrophotometer. It is preferable for transmissivity to be measured using two more types of calibrating optical glass filters of different transmissivity. In the measurement of the transmissivity of an actual sample, the accurate transmissivity can be found by subtracting the instrumental error from the measured value in order to correct the instrumental error inherent in this spectrophotometer.

It is also possible to calibrate the absorbance graduations in the high absorbance region by employing a so-called multi-filter approach, in which two or more filters are stacked.

[Examples]

The present invention will now be further described through examples, but is not limited to or by these examples.

<u>Example 1</u>

(1) Production of optical glass filters

Ortho-phosphoric acid (in the form of an aqueous solution) <u>having a purity high enough to permit use as a raw material for manufacturing glass</u> [Translator's note: The underlined phrase may modify all the listed compounds; it is impossible to tell from the original], aluminum hydroxide, aluminum fluoride, barium fluoride, strontium fluoride, calcium fluoride, magnesium fluoride, lithium carbonate, lithium fluoride, and so forth were used as raw materials (this does not exclude the use of compound oxides such as aluminum phosphate as a raw material). A mixture of the above raw materials was put in

a platinum crucible and melted at between 800 and 1000°C, the melt was stirred until homogeneous, and any bubbles were removed, after which the molten batch was cast into a mold preheated to a suitable temperature, and slowly cooled, which produced four different glass filters (Nos. 1 to 4) with the compositions shown in Table 1.

Table 1

Sample No.	1	2	3	4	Commercially available ND filter
P_2O_5	11.0	23.0	27.0	32.2	
Al_2O_3	3.0		5.0	2.4	2.0
AlF_3	28.0	20.0	10.0	7.5	
BaF_2	12.0	25.0	15.0		
SrF_2	20.0	15.0	15.0	12.2	
CaF_2	16.0	12.0	11.0	1.0	
MgF_2	7.0	5.0	6.0	0.4	
Li_2O			5.0		
LiF			6.0		
NaF	3.0				
BaO				40.0	
MgO				4.3	
CeO_2	0.008	0.01	0.1	0.1	
SiO_2					62.0
B_2O_3					19.0
K_2O					10.0
Na_2O					4.0
ZnO					5.0
Cr_2O_3	0.15				
Fe_3O_4					3.0
Co_2O_3	0.005				0.04

(2) Measuring the spectral transmissivity of the obtained optical glass filters

Fig. 1 shows the spectral transmissivity curves for the glass filter Nos. 1 to 4 obtained in this example and for a commercially available ND filter (whose composition is given in Table 1) at a thickness of 2 mm.

It can be seen from Fig. 1 that the commercially available ND filter reached zero transmissivity in the vicinity of 350 nm, and did not transmit light of any shorter wavelength, whereas the glass filter Nos. 1 to 4 of this example had relatively flat transmissivity curves at 200 to 300 nm, which made them favorable for calibrating transmissivity or absorbance in the ultraviolet region.

<u>Example 2</u>

(1) Production of optical glass filters

Four different optical glass filters (Nos. 5 to 8) were produced using various raw material compounds just as in Example 1 (1). The compositions of glass filter Nos. 5 to 8 were similar to that of the above-mentioned glass filter No. 2, but the 0.01% amount of CeO_2 was changed to 0.008% (No. 5), 0.016% (No. 6), 0.029% (No. 7), and 0.053% (No. 8), while the amounts of the other glass components, namely, P_2O_5, AlF_3, BaF_2, SrF_2, CaF_2, and MgF_2, were the same as in the glass filter No. 2.

(2) Performance testing of the obtained optical glass filters

Examples of qualities demanded of a calibrating filter include a stable transmissivity value, a low temperature coefficient, and good durability with respect to

deterioration caused by UV exposure light. The following tests were conducted with these in mind.

① Test for transmissivity stability

The optical glass filter Nos. 5 to 8 were each cut to a size of 10 × 10 × 35 mm and placed in a cuvette type holder. Each of these was mounted in the sample cell of a calibrating spectrophotometer, transmissivity measurement at various wavelengths was repeated a number of times, and the repeatability of the measured values was examined. These results are given in Table 2.

Table 2

Measured wavelength / Sample	207nm	211nm	222nm	229nm
No. 5	60.131±0.049	60.690±0.042	57.220±0.068	58.696±0.060
No. 6	52.486±0.042	53.287±0.037	46.669±0.062	48.356±0.040
No. 7	27.617±0.060	28.382±0.066	26.147±0.070	31.040±0.075
No. 8	25.986±0.0283	27.104±0.036	20.068±0.058	21.833±0.054

235nm	237nm	263nm	280nm
56.891±0.033	55.088±0.051	55.366±0.080	60.132±0.100
44.857±0.032	37.592±0.061	36.991±0.075	42.004±0.084
27.548±0.024	19.566±0.019	18.804±0.025	23.318±0.051
17.851±0.038	9.739±0.042	8.993±0.044	11.713±0.061

The transmissivity repeatability tended to be worse the higher was the measured transmissivity of the filter and the longer was the measured wavelength. The magnitude of this variation, however, was at most 0.17%, and averaged 0.1% or less, as revealed by the ratio to the average value of the measured transmissivity (coefficient of variation).

In contrast, variance in transmissivity due to repeated preparation of the potassium dichromate solution was confirmed to be no more than 0.33% as the difference in transmissivity attributable to preparation three times at a high concentration. This figure corresponds to about 1% with respect to the measured transmissivity, so the excellence of the optical glass filter of the present invention in relation to stability of measured values is clear.

② Temperature test

The transmissivity of the optical glass filter No. 7 was measured at temperatures of 10°C and 50°C, and the effect that temperature had on transmissivity was examined. These results are shown in Fig. 2. As to the effect of the temperature of a UV filter on transmissivity, a distinctive temperature characteristic was observed, whereby there is a so-called isosbestic point in the spectrum, which is a wavelength that is unaffected by temperature, with transmissivity increasing along with temperature at wavelengths longer than this, and decreasing on the shorter wavelength side.

More precise measurements revealed that this temperature isosbestic point (P) is present near 250 nm, and does not vary with the type of filter. Nevertheless, the change in transmissivity due to temperature is at most only about ±0.01%/°C, so it was found that in ordinary measurement work the effect of temperature on the measured values can be ignored if temperature changes during measurement are minimized.

③ Test for deterioration due to UV exposure

A test was conducted as set forth in Japan Optical Glass Industrial Standard JOGIS-04, and as a result no change was noted in transmissivity over the entire region from 200 to 400 nm.

The above test results confirmed that the optical glass filter Nos. 5 to 8 of Example 2 are favorable as filters for calibrating transmissivity or absorbance in the ultraviolet region. Furthermore, the optical glass filter Nos. 1 to 4 of Example were subjected to the ① Test for transmissivity stability, ② Temperature test, and ③ Test for deterioration due to UV exposure in the same manner, and the obtained results were similar to those for the optical glass filter Nos. 5 to 8 of Example 2.

[Merits of the Invention]

As detailed above, the filter of the present invention has a gently sloping transmissivity curve over the entire region from 200 to 300 nm in the ultraviolet region, and has other advantages, such as the following.

(1) The accuracy and repeatability of measured values are good.

(2) Temperature has little effect, and an isosbestic point can be utilized for the calibration wavelength.

(3) Glass that can be obtained at low cost is used, and the filter is easy to handle and maintain.

Therefore, this filter can be used to advantage for the calibration of transmissivity or absorbance in the ultraviolet region.

4. **Brief Description of the Drawings**

Fig. 1 is a graph of the transmissivity of the glass filter Nos. 1 to 4 of the present invention and of a commercially available ND filter; and

Fig. 2 is a graph of the change in the transmissivity of the glass filter No. 7 of the present invention versus temperature.

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Figure 1

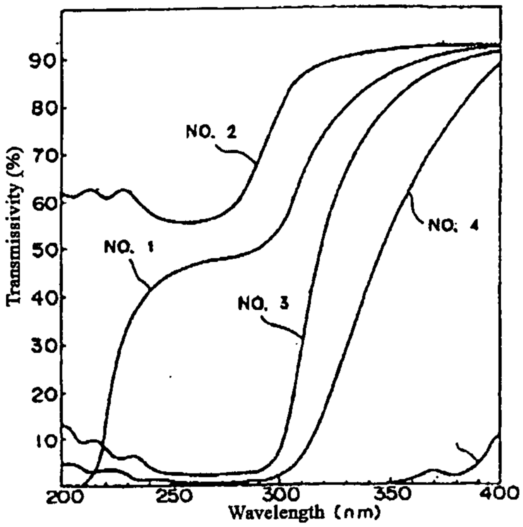

Figure 2